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X-RAY SPECTROSCOPIC STUDIES OF THE SOLID STATE

Technical Report No. 1

K SPECTRA OF POTASSIUM CHLORIDE

by

L. G. Parratt and E. L. Jossem

June 20, 1954

**Physics Department
Cornell University
Ithaca, New York**

A report of research supported by the Office of Naval Research and by the United States Air Force through the Office of Scientific Research of the Air Research and Development Command.

**O.N.R. N6-ori-91 T.O.1
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X-Ray Spectroscopy of the Solid State
Potassium Chloride*

by

L. G. Parratt and E. L. Jossem
Cornell University
Ithaca, N. Y.

Abstract

The K β spectral regions of both potassium and chlorine in crystalline KCl present experimentally a much more complex array of structure, both in emission and in absorption, than can be explained by the conventional energy level diagram for the solid state. The difficulties seem to arise from a pre-occupation with one-electron transitions between states described by an incomplete consideration of electron configurations.

When one considers the various probable electron configurations of the many-electron solid system, one finds additional initial and final states. Several different energies are present for the K state (1s vacancy), only one of which is significantly involved in emission but all of which are necessary to explain absorption. The difference in the K configurations is in the distribution of charge density represented by the outer electrons, those electrons near the valence band in KCl. Suddenly confronted with the problem of screening the excess positive charge attending a 1s vacancy, the charge density in the outer bands redis-

*Supported in part by the U.S. Office of Naval Research and in part by the U.S. Air Force through the Office of Scientific Research of the Air Research and Development Command.

tributes itself, distorting the bands, and, in KCl, establishing one or more local discrete levels below each band. With the filled discrete levels below the 3p band, the narrow intense β_1 line is explained; with the normally empty discrete levels below the conduction band, the narrow intense absorption lines are explained.

The discussion given is primarily experimental and phenomenological. The qualitative agreements are very satisfactory, but a quantitative theoretical treatment is obviously needed.

Introduction

In x-ray spectroscopy of the solid state it has been presumed that the outer "levels" involved are the energy bands characteristic of the solid as a whole. The emission spectrum near a series limit and the absorption spectrum near an absorption discontinuity are presumed to give the energy position, width, and density of states of the valence and conduction bands¹.

As an example, the pertinent transitions in the K spectra of crystalline potassium chloride are indicated in the conventional energy level diagram sketched in Fig. 1. The 1s, 2s, and 2p states are narrow in energy. The full width at half maximum of the 1s state (width due to the lifetime of the state) is about 0.45 ev

1. E.g., see H.W.B. Skinner, Phil. Trans. Roy. Soc. (Lond.) A239, 95 (1940); H.M. O'Bryan and H.W.B. Skinner, Proc. Roy. Soc. (Lond.) A176, 229 (1940); Y. Cauchois, Les Spectres de Rayons X et la Structure Electronique de la Matiere, 1948, Gauthier-Villars, Paris; and H. Niehrs, Ergebnisse der Exakten Naturwissenschaften 23, 359 (1950).

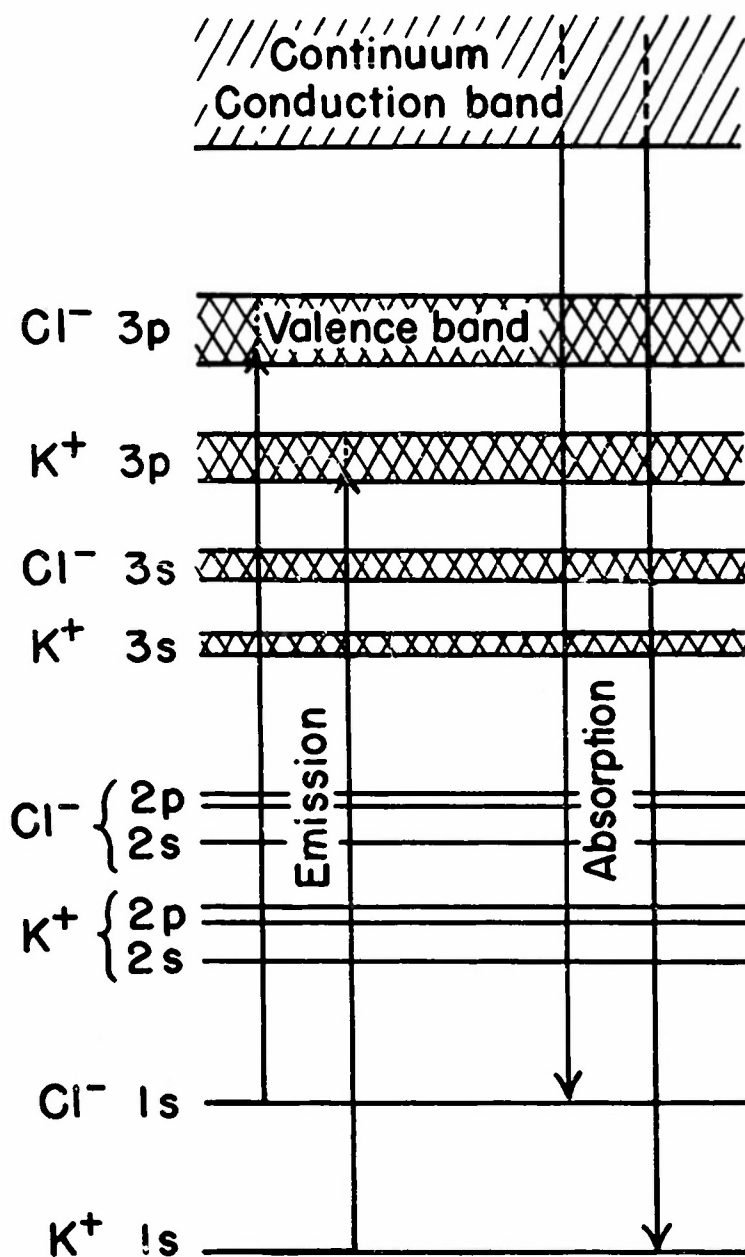


Fig. 1. Conventional x-ray energy level diagram (schematic) for crystalline KCl. The arrows point from the initial to the final states. (This diagram is incomplete, see text.)

for chlorine and about 0.73 ev for potassium². The 3s and 3p states are much broader because of the effect of overlapping electronic wavefunctions of neighboring atoms in the solid. The 3p valence band at half maximum of the density-of-states curve is estimated to be about 2 ev wide³. The continuum consists of all the overlapping normally empty bands (4s, 3d, 4p, etc.).

Transition arrows in Fig. 1 are presumed to give directly the energy released or absorbed as the system changes radiatively from an initial to a final state. The width and shape of the $1s \rightarrow 3p$ (or $K \rightarrow M$) emission, when corrected for the resolving power of the spectrometer and for the $1s$ width, should give essen-

2. Direct measurement of the $1s$ width for metallic potassium (J. Platt, Phys. Rev. 69, 337 (1946)) gives 0.75 ev, or 0.73 ev after correction for the resolving power of the spectrometer. The corrected $1s$ width for gaseous argon (L.G. Parratt, Phys. Rev. 56, 295 (1939)) is 0.58 ev. These two $1s$ widths are in excellent agreement with the theoretical prediction of proportionality with the square of the energy of the state. (The metallic potassium absorption discontinuity is apparently free from perturbing unresolved fine structure.) For chlorine we extrapolate and obtain the $1s$ width as 0.45 ev. The width of each of these three $1s$ states is believed to be correct within about 0.05 ev.

3. The authors do not know of a reliable calculation of the theoretical widths of the 3p bands in KCl. However, W. Shockley, Phys. Rev. 50, 754 (1936), calculated that the chlorine 3p band in NaCl is about 4.4 ev wide, and P. Löwdin, A Theoretical Investigation into Some Properties of Ionic Crystals (Almqvist and Wiksells Boktryckeri AB, Uppsala, 1948), calculated the spatial extents of the electronic wavefunctions for both KCl and NaCl. From these considerations, we conclude that the chlorine 3p and potassium 3p bands in KCl are about 4.4 and 3.4 ev wide respectively. These widths refer to the "base" of the density-of-states curve. The theoretical shape of the density-of-states curve rises perhaps as $E^{1/2}$ near the bottom and perhaps as $E^{3/2}$ near the middle, reaches a maximum, then descends more steeply on the high energy side. Hence, the theoretical width at half maximum of the chlorine and potassium 3p bands may be about 2 and 1.5 ev respectively.

tially the width and shape of the density-of-states curve for the valence band if the transition probability is uniform over the band. The difference in the energy position of the high energy side of the (corrected) emission, and of the low energy side of the (corrected) absorption edge, has been presumed to give the energy gap between the 3p band and the continuum. And, also, the shape of the absorption discontinuity and the position and shape of any component structure in the absorption spectrum should tell us the density of energy states (multiplied by the transition probabilities) presumably in the continuum.

In the present paper these relations are studied quantitatively for potassium and chlorine in crystalline KCl. We shall conclude that the conventional interpretations of the diagram of Fig. 1 are not adequate -- we must introduce "impurity-type" levels (and states) which arise as a consequence of the 1s vacancy⁴.

Emission Spectra

The observed emission for chlorine and for potassium in crystalline KCl are shown as part of Fig. 2. The strong emission line in each case is known as the K β_1 line; the less intense structure on the high energy side of each β_1 line has been called by the non-committal name of "satellites".

4. L.G. Parratt and E.L. Jossem, Phys. Rev. 84, 362 (1951), 85, 729 (1952); and J. Friedel, Phil. Mag. 43, 153 and 1115 (1952).

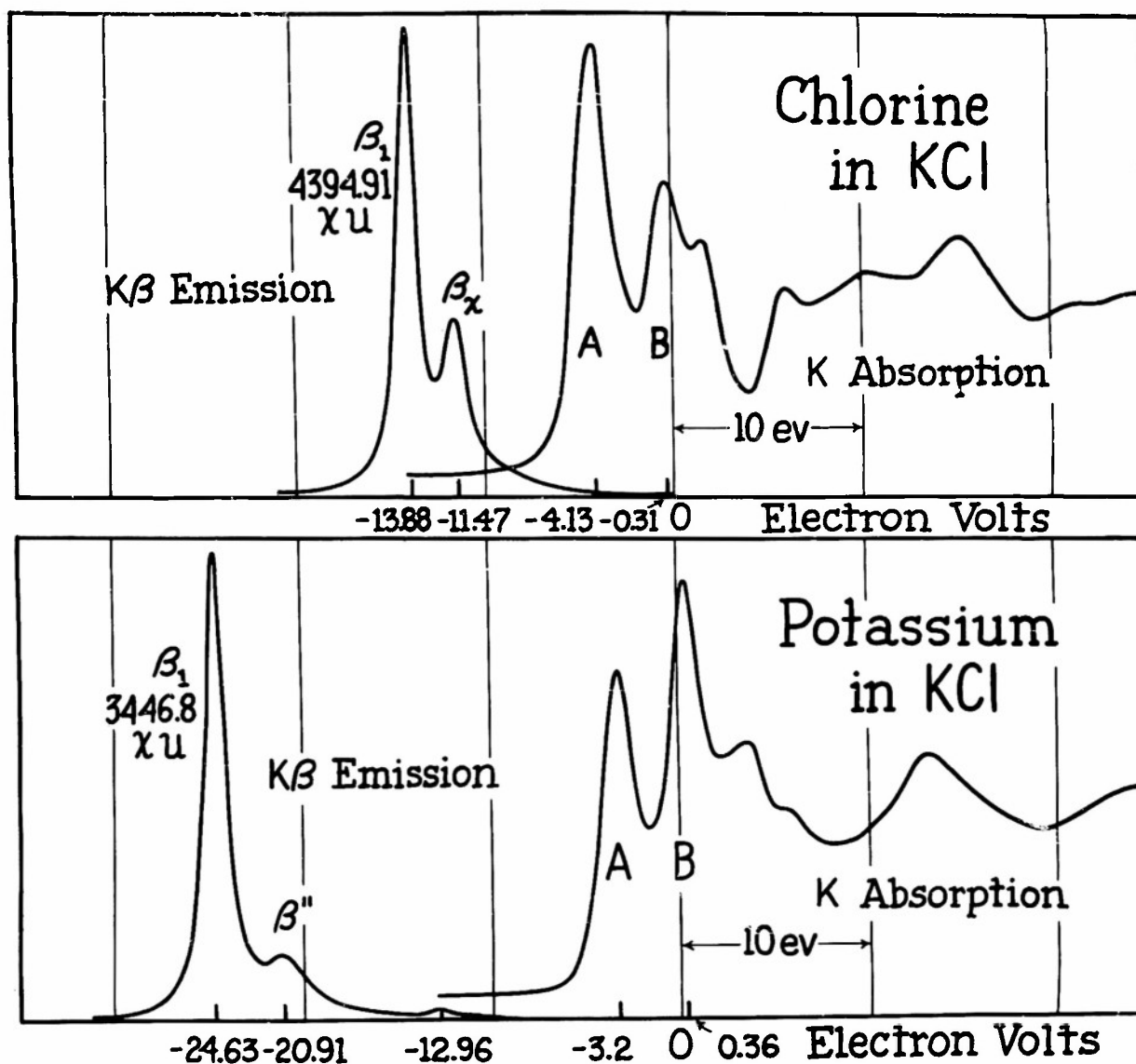


Fig. 2. Experimental emission and absorption spectra, involving the valence and conduction bands as shown in Fig. 1. The complexity of the spectra requires additional states which are not shown in Fig. 1.

The KCl curves were recorded with a focusing crystal spectrometer⁵ and also with a two crystal spectrometer⁶. Excellent agreement was obtained between the curves recorded with the different x-ray tubes and instruments.

With each spectrometer, a proportional counter system, with a single channel discriminator having a narrow channel width, served very satisfactorily for measuring intensity. This system also discriminated effectively against background intensity (higher-order Bragg reflection, scattered photons of different energy, etc.), a feature of great importance in accurate studies of extremely faint intensities.

With the focusing instrument, a bent mica crystal was used in third order reflection for chlorine and in fifth order for potassium. With the two crystal instrument, calcite crystals⁷ were used in the (1, +1) position.

The x-ray tube target, with each spectrometer, consisted of a layer of KCl condensed by vacuum evaporation on a water-cooled nickel substrate (or copper or aluminum -- no effect of the substrate was found). The evaporation and condensation were carried out at a pressure always lower than 10^{-6} mm Hg, in the same

5. E.L. Jossem and L.G. Parratt, Phys. Rev. 79, 210 (1950).

6. L.G. Parratt, Phys. Rev. 54, 99 (1938), and references. The absorption curves of Fig. 2 are reproduced from J.W. Trischka, Phys. Rev. 67, 318 (1945), and the relative positions of their essential features have also been checked with the focusing spectrometer.

7. These crystals were calibrated as to their reflectivities and designated A⁴B⁴ by L.G. Parratt, Rev. Sci. Instr. 6, 387 (1935). After 1935, they deteriorated somewhat upon standing in atmospheric air, and were again ground, polished and etched in 1939. Since 1939, they have again become somewhat imperfect (the (1, -1) widths are a little wider than in 1935) but are still Class I crystals.

vacuum as used in the x-ray generation. Except during evaporation, the x-ray vacuum was always less than 3×10^{-7} mm Hg. With these targets, an irregular decrease of intensity with time was observed for both the chlorine and potassium emission, and this time dependence introduced an uncertainty of a few per cent in the relative intensities of various regions of each curve during, say, a two-hour run⁸. Many curves were recorded and averaged.

With 14 kv across the x-ray tube, and with 5 ma tube current, the counting rate at the peak of chlorine β_1 with a fresh thick target was about 500 counts per second with the detector slit of the focusing spectrometer set at 0.0065 mm (0.1 xu) in width. Under the same conditions (including the absorption path) the

8. The time-dependence of the intensity, usually a few per cent per hour, may have been caused by a target deterioration (stripping of the KCl from the substrate by electron bombardment and consequent local heating) or by a target contamination layer of either (a) decomposed oil from the diffusion pumps or other "vacuum" residues, or (b) tungsten evaporated from the filament. An effort was made to reduce the oil backstreaming from the pumps, as already described by L.G. Parratt and E.L. Jossem, Rev. Sci. Instr. 23, 188 (1952), and a liquid-nitrogen-cooled bulb was suspended in the vacuum chamber of the x-ray tube. The filament consisted of a "soda straw" spiral $3/4$ " long and $1/8$ " diameter formed from a tungsten ribbon $1/16$ " wide, 0.002" thick and about 3 inches long. The large surface for electron emission allowed operation at a rather low temperature to reduce the tungsten contamination on the target. A run with a good metal target (palladium or antimony, whose $L\alpha_1$ line was used as a secondary reference) gave constant $L\alpha_1$ intensity within 0.5% for more than a few hours, so we believe the irregular decrease with KCl is caused by target deterioration rather than by contamination.

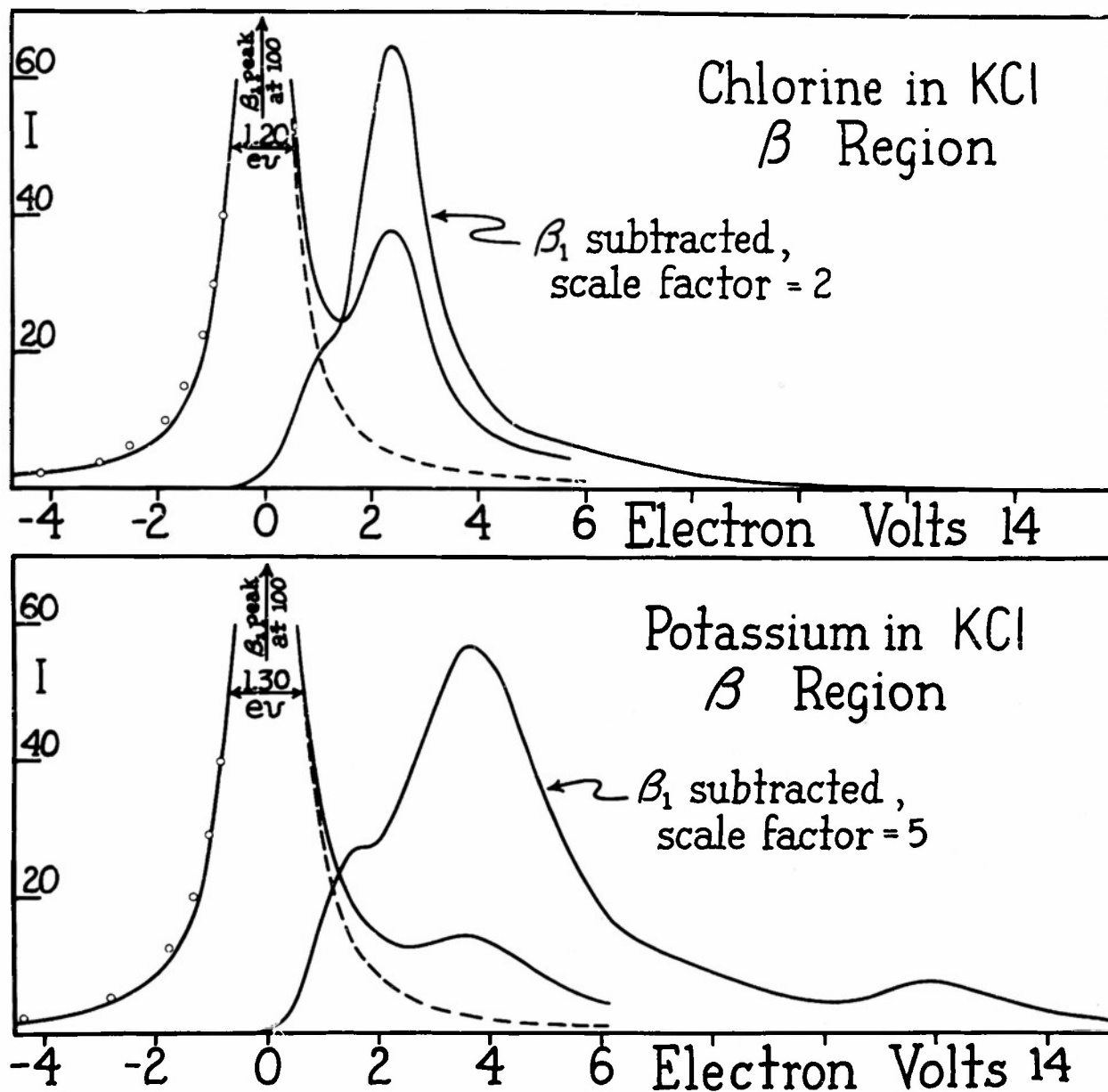


Fig. 3. Intensity in the β region after subtraction of the β_1 line. The β_1 was arbitrarily assumed to be symmetrical about the observed peak intensity.

The classical dispersion shape, matched at the peak and at the half maximum points, is indicated by the open circles on the low energy side of β_1 .

These curves were recorded with the two crystal spectrometer.

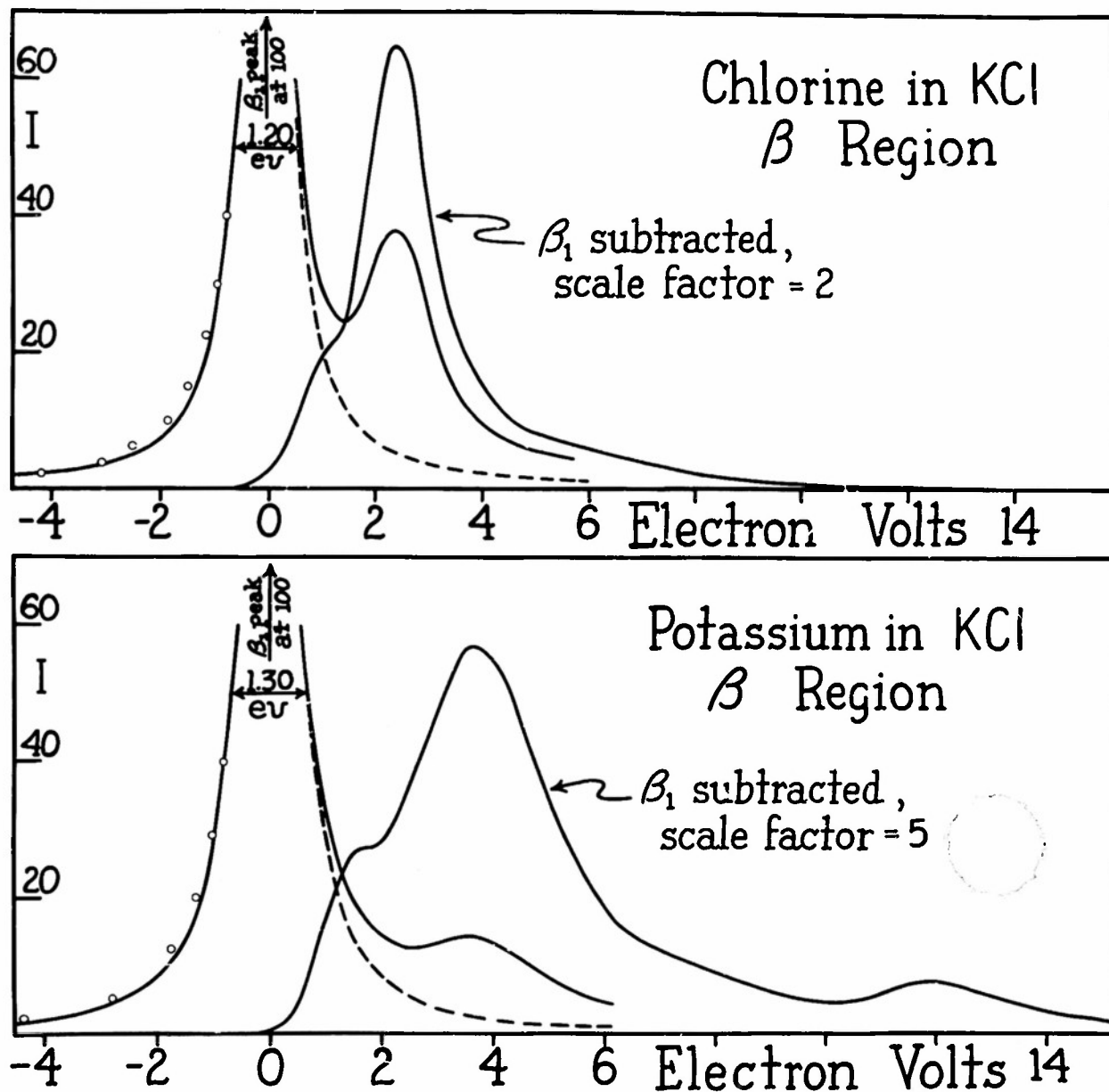


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These curves were recorded with the two crystal spectrometer.

counting rate with the two crystal spectrometer was 900⁹.

In Fig. 3 the strong β_1 line has been subtracted from the observed emission contour. The shape of the β_1 line was arbitrarily assumed to be symmetrical about the observed intensity peak.

The shapes of x-ray lines are often compared with the classical dispersion curve

$$I = \frac{P}{1 + \left(\frac{\Delta E}{W_{1/2}}\right)^2} \quad (1)$$

where ΔE , the incremental energy abscissa, is zero at the peak intensity P and equal to $W_{1/2}$ at half maximum intensity. The open circles on the low energy side of β_1 in Fig. 3 are plotted from Eq. (1). The observed β_1 shape in this region is typical of x-ray lines in general.

Experimental Width of the Final State in β_1 Emission. With the focusing spectrometer, the observed full width at half maximum intensity of the β_1 line is 1.68 ev for chlorine and 1.33 ev for

9. The lower luminosity of the focusing spectrometer is partially explained by the very narrow slit used. The resolving power was only slightly reduced by increasing the slit width from 0.1 xu to 0.35 xu; with the wider slit the counting rate was increased to about 1,600. However, the opening at the bent crystal limited the maximum perpendicular cross-section of the beam to 1.5 x 0.4 cm whereas the beam with the two crystal spectrometer was somewhat smaller, 0.8 x 0.6 cm, in cross-section. We conclude that the reflectivity of the mica at this wavelength in third order is about the same as that of the two calcites in series, but, as noted in footnote 12, the resolving power is considerably less.

potassium¹⁰. To deduce the width of the final state in this emission, corrections must be made for (a) the resolving power of the spectrometer and (b) the width of the initial 1s state.

The "spectral window" of a focusing spectrometer is determined by a combination of the crystal diffraction pattern, the focusing defects, and the width of the detector slit. This combination is unknown.

The resolving power of the two crystal spectrometer is much better understood. With this instrument the width correction is given by the formula^{11, 12}

$$W_t = W_o - 2.9 W_c^{1.7} \quad (2)$$

where W_c is the width of the (1, -1) curve, W_o is the observed width of the line whose true width is W_t (all widths in xu). For the chlorine β_1 line, corrected for the overlapping β_x , $W_o = 1.87$, $W_c = 0.414$ and W_t computes to be 1.22 xu or 0.78 ev. Likewise, W_t for the potassium β_1 is 0.95 ev.

The correction for the width of the initial 1s state is easy if we make the assumption that the shape of the β_1 line and the shape of the 1s state are each given by a classical

10. These widths are measured after the small correction for the β_x or the β'' complex, as illustrated in Fig. 3 for curves recorded with the two crystal spectrometer.

11. L.G. Parratt, ref. 7.

12. The numerical resolving power, $\lambda/\Delta\lambda$, of the focusing spectrometer can be approximated as follows. From the observed W_o for $Cl^- \beta_1$ and the known W_c from the two crystal measurements, W_c is deduced from Eq. (2) as 0.64 x". Taking $\Delta\lambda = W_c$, we find $\lambda/\Delta\lambda = 6,870$ for the chlorine β_1 wavelength in third order reflection. The same procedure gives $\lambda/\Delta\lambda = 11,500$ for the potassium wavelength in fifth order.

dispersion curve, Eq. (1). In this case, the observed line width is the simple sum of the widths of the initial and final states¹³. The observed β_1 line is very nearly classical dispersion in shape on the low energy side where there is no obvious unresolved structure; on the high energy side the structure prevents a comparison below near the half maximum¹⁴. Theory predicts that any singlet, atomic state is classical in shape. It is believed that no great error is made in taking the width of the final state as the simple difference between W_t and W_{ls} .¹⁵ Then, for chlorine, $W_{3p} = 0.78 - 0.45 = 0.33$ ev, and for potassium $W_{3p} = 0.95 - 0.73 = 0.22$ ev, with an uncertainty of less than about 0.1 ev in each case.

The narrow final states, having nearly classical dispersion shapes¹⁵, cannot be reconciled with the broad 3p bands of the crystalline KCl solid¹⁶. We conclude that the β_1 emission cannot

13. E.g., see Richtmyer, Barnes and Ramberg, Phys. Rev. 46, 843 (1934), and L.G. Parratt, ref. 6.

14. Confidence is established in the above use of Eq. (2) by the fact that the observed β_1 contour above the half maximum is essentially the same as the α_1 shapes for which the formula was specifically devised.

15. We cannot safely conclude, however, that the shape of the 3p final state in β_1 emission is also classical dispersion, but it cannot be far different, especially below its half maximum where we are particularly interested.

16. Previous measurements of the β_1 line, e.g., J. Valasek, P. R. 53, 274 (1938), with lower resolving power and the less accurate photographic method of intensity measurement, have also implied a similar width discrepancy. O'Bryan and Skinner, ref. 1, give a calculated "Sommerfeld band width" of 4.2 ev for the chlorine 3s band in KCl (expected to be much less wide than the 3p band (see footnote 3)) and discuss an observed $2p \rightarrow 3s$ chlorine line of width 0.65 ev. No particular point, however, has been made of this discrepancy heretofore, perhaps because of unsatisfactory accuracy in the width measurements.

be represented by the transition arrow in Fig. 1 if the arrow terminus is allowed to range throughout the broad 3p band. We therefore re-examine the emission process.

The Emission Process: Many-Electron System. In a free gaseous atom, the energy of the ground state is taken to be zero. This, incidentally, is the initial state for x-ray absorption. The ejection of an inner, say, a 1s, electron causes the atom to shrink -- all the outer electrons, now in a stronger electrostatic field, move to positions closer to the nucleus. This is the initial state for emission and is also the final state for absorption. The energy of this 1s state must, of course, take into account the new positions of all the electrons. Upon emission of an x-ray photon, the inner vacancy is filled and another vacancy is produced farther out in the atom. All the electrons again move to new positions, and the energy of the final state must take into account all the new final positions. A radiative emission process involves the simultaneous motion of all the electrons in the gaseous atom, and the observed photon energy is a narrow single line only if the changes in the electronic configurations are the same for all the emitting atoms.

When the atom is part of a solid, the wavefunctions of its electrons interact with those of neighboring atoms. The system which must now be considered includes all the electrons of all the atoms in the solid. Fortunately, interaction between the inner electrons of neighboring atoms is usually negligible so that only the outer electrons of those atoms not suffering the 1s vacancy are seriously involved.

When an inner vacancy occurs, the electrostatic field of

the unscreened nuclear charge is certainly felt throughout the atom suffering the 1s vacancy, and, in principle, may extend a few atomic diameters away from the vacancy site. The theoretical description of the system containing an electron vacancy depends upon the model used. The difficulty with almost all treatments to date is that they have been based essentially on the one-electron-approximation.

Heitler-London Model. One description is offered by the Heitler-London model. With an inner electron vacancy, those electrons (and levels) previously contributed to the normal solid-state bands by the atom which now contains the inner vacancy (and perhaps by a few neighboring atoms) may be extracted from the normal solid-state bands and occupy local, discrete levels¹⁷. These new levels are probably just below the "mother" bands. However, a few atomic diameters away from the vacancy site the solid-state bands remain essentially unperturbed.

Some clarification (not without danger of oversimplification, however) may be afforded by the following argument. Consider an otherwise normal KCl crystal to have a very large lattice spacing. The wavefunctions of the electrons of neighboring atoms have negligible mutual interactions and the energy levels of all the like-atoms are sharp and of the same energy value. Suppose now

17. The atomic site containing the inner vacancy, so far as the outer electrons and neighbors are concerned, is an impurity-type atom of nuclear charge increased by about unity.

Similar n-type impurity levels are discussed by J.C. Slater and W. Shockley, Phys. Rev. 50, 705 (1936), G.H. Wannier, Phys. Rev. 52, 191 (1937), J.C. Slater, Phys. Rev. 76, 1592 (1940), H.W. Leverenz, An Introduction to Luminescence of Solids (John Wiley & Sons, 1950), and by others, e.g., ref. 4.

that one of the atoms contains a 1s vacancy. All the energy levels of this atom lie below their otherwise normal positions. For such a case, with a chlorine atom suffering the 1s vacancy, the outer levels are sketched qualitatively in Fig. 4. If the lattice spacing is reduced¹⁸ to the normal crystal 6.23 Å spacing, the ionization level (marked a) persists below the normal 3p level, even as the normal level broadens into the solid-state band. And, in addition, new ionization levels (marked b and c) are shown "peeling off" the bottom of the 3p bands of both chlorine and potassium. As discussed later, these b, c levels arise only if the field of the excess positive charge extends appreciably to neighboring atoms.

Included in the figure is a level marked A which may be occupied (perhaps by the previous 1s electron in an absorption process). Since the electron is still bound to the atom, the A level is indicated as an excitation level¹⁹. In this model, the A, B levels are actually two of several series of levels, 4s, 5s ..., 4p, 5p, ..., 3d, 4d, ..., etc.; for simplicity, only two levels are shown, A and B, presumably the 4p and 5p (considering the selection rules and our later absorbing interest in transitions to the 1s state).

18. The lattice spacing must be reduced in a time short compared with the lifetime of the 1s vacancy (but with adequate time for the bands to form). The 1s lifetime is 1.5×10^{-15} seconds for chlorine and 9×10^{-16} seconds for potassium, as deduced from the uncertainty relation $\Delta E \Delta t \approx h/2\pi$).

19. F. Seitz, The Modern Theory of Solids (McGraw-Hill, 1940), p. 96, and Wannier, ref. 17.

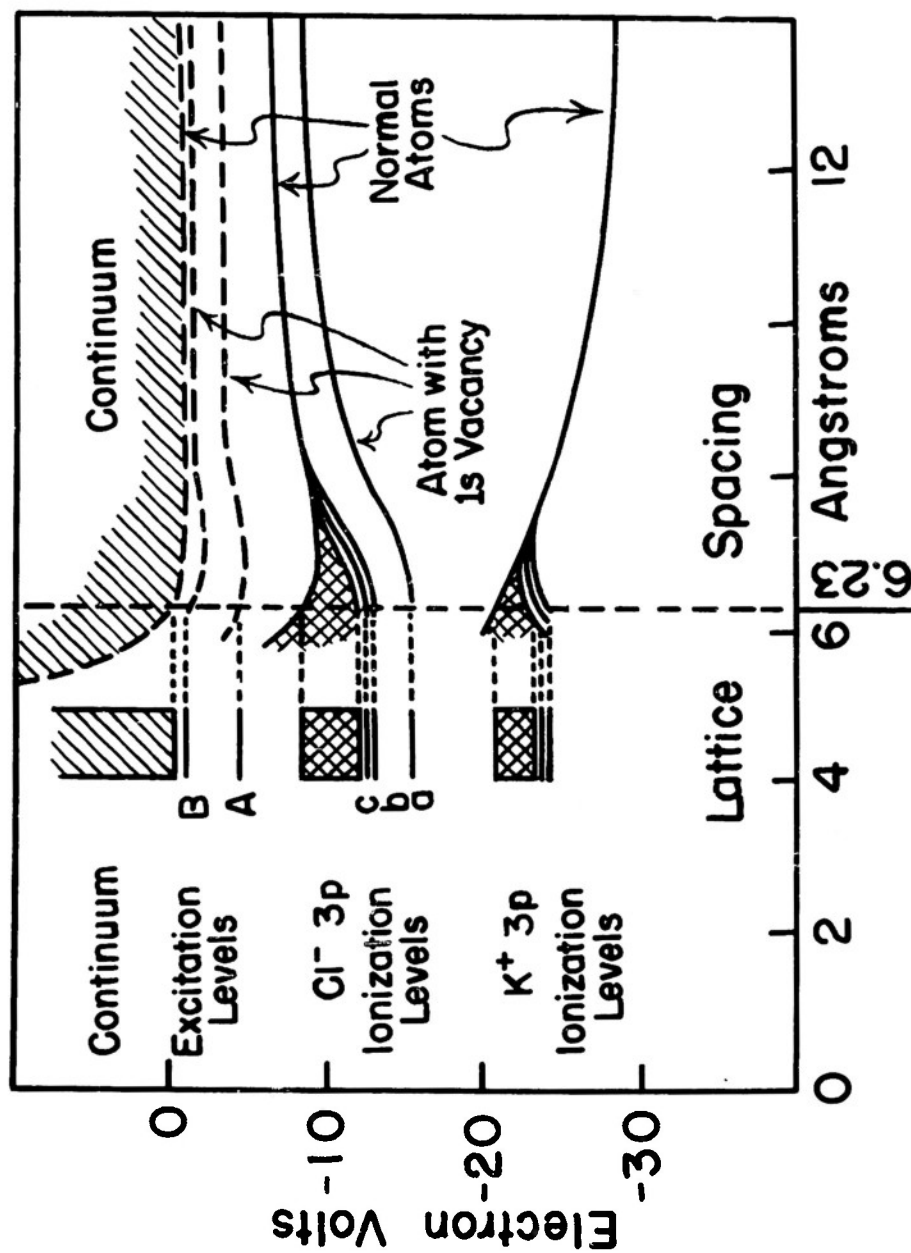


Fig. 4. Outer electron levels for normal atoms and for an atom with a 1s vacancy in KCl crystal. At the equilibrium lattice spacing, 6.23 Å, levels a, b, c, \dots , and A, B, \dots arise when one 1s electron has been removed. A different set of a, b, c, \dots and A, B, \dots levels (not shown) arises if the 1s vacancy is in a potassium atom.

Also, it may be noted that, notwithstanding the suggestion in the figure, the limit or head of the a, b, ... series or of the A, B, ... series may possibly lie within the "mother" band rather than at its bottom edge.

The coulomb field of the unshielded nuclear charge decreases roughly as $e/(\epsilon_0 r^2)$ where ϵ_0 , the effective dielectric constant, has a value between unity and the bulk high-frequency value (2.13 for KCl). In principle, as also stated above, this electrostatic field, superposed on the periodic lattice field, may extend with sufficient strength to neighboring atoms to bind electrons in a level whose wavefunction extends over a few atomic spacings.

Since the orbital radius of the electron in an A level may be of the order of an atomic distance, this level may also be thought of as a near-neighbor level. It is immaterial now whether the A and B levels are thought of as the 4p and 5p levels, as near- and next-near-neighbor levels, or as the first and second "exciton" hydrogenic p levels in which the electron is bound simply to the relatively immobile 1s hole¹⁹.

Another rough sketch of these possible electronic configurations is shown in Fig. 5, again with danger of oversimplification. The regions of large amplitude of the electronic wavefunctions are presumably those where the height or darkness of the level or band is large. In positioning the A and B orbits in Fig. 5, consideration has been given to the electron attraction and repulsion of the potassium and chlorine atoms respectively.

Collective Electron Model. The configuration of the outer electrons attending a 1s vacancy is much more complex than indi-

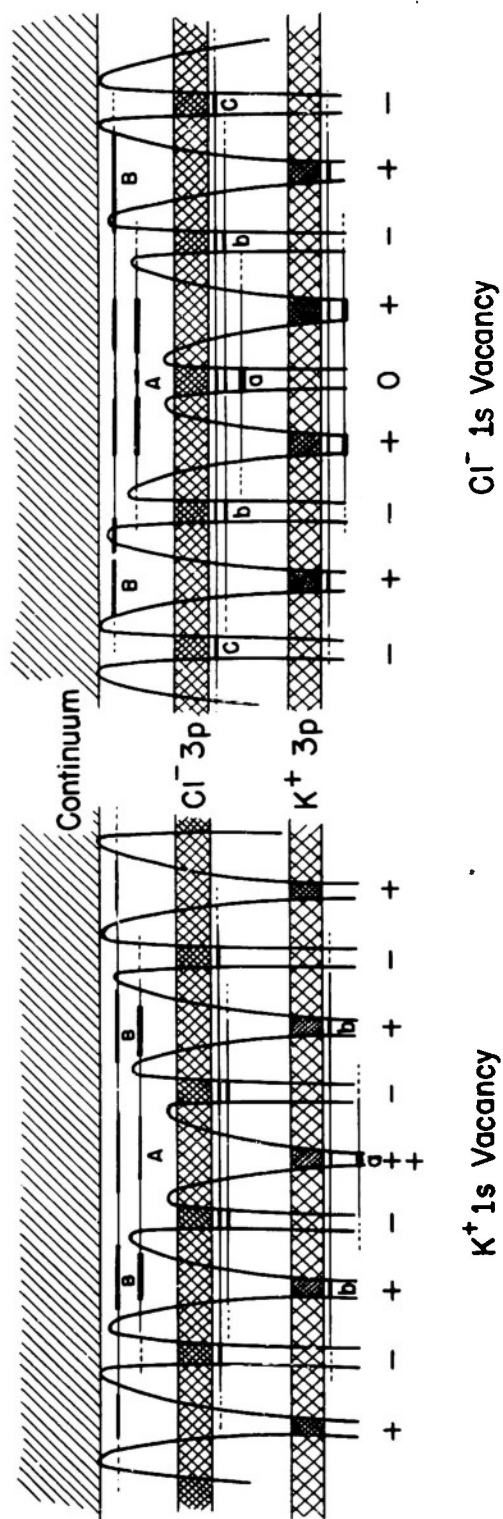


Fig. 5. Rough sketch of generalized electron configuration for crystalline KCl with a 1s vacancy in either potassium or chlorine.

cated in the previous section. For example, the Heitler-London model would have six 3p electrons in each of the a, b, c levels. In the collective electron model, perhaps one or two electrons drop into the discrete a level in the system's effort to screen the bared nuclear charge, with the remaining screening accomplished by a local distortion of the bands themselves. It is possible, for some combinations of atoms, inner vacancy, and solid, that no electrons drop into the discrete level below the valence band, the screening at this distance from the center of the atom being accomplished entirely by the altered charge density in the valence band. A somewhat analogous situation has been discussed²⁰ for a metal, or any conducting solid, in which the redistributed charge in the valence band may screen so completely that the A, B levels do not form.

In the case of an ionic crystal, such as KCl, the charge flow in the bands is probably not very great and the a and A, B levels are of real significance. But, it should be pointed out, the wave-function symmetry of these levels may not be simple p-type. Each level may come not simply from extraction from the mother band, but may be a linear combination of all levels or bands above it and may have a mixed wavefunction symmetry.

Initial Energy State. It may be inferred from the above discussion that several different electron configurations are possible with a 1s vacancy. The energy of the 1s state may also be split since the energy depends on the configuration. For

20. J. Friedel, ref. 4.

example, the A level for chlorine may lie sufficiently close to the valence band that, in the scramble of electrons attending the formation of the 1s vacancy, a valence electron may jump to the A level with a probability such that for some atoms the jump may occur and for others not. Or the number of electrons dropping into the a level may be statistically different. We don't know these relative probabilities. However, it can be definitely concluded experimentally²¹ that, if more than one 1s energy state exists, so far as emission is concerned, they are extremely close together. We shall assume that only one 1s state exists for emission although we cannot at this time definitely describe its electron configuration.

Fig. 6 shows schematically five possible electron configurations, two of which include a 1s vacancy. Each configuration has its characteristic energy state. We have arbitrarily chosen one of the two K(1s) states as the significant 1s state for emission.

Final Energy State. We now turn to the final energy state which exists in KCl after a radiative transition in the β spectral region has occurred. Since the 1s vacancy is no longer present,

21. The 1s vacancy state is the initial state for emission of the $K\alpha_{1,2}$ lines whose structure and widths have been very accurately measured. Each of these lines is a singlet whose width is not a sensitive function of atomic number or physical state of the target of the x-ray tube. (E.g., see L.G. Parratt, Phys. Rev. 50, 1 (1936), Table VI, and references. Also, see the comparison of the 1s width of metallic potassium with gaseous argon, footnote 2). The small dependence of width, observed in some instances, is probably caused by effects in the L_{II,III} final states.

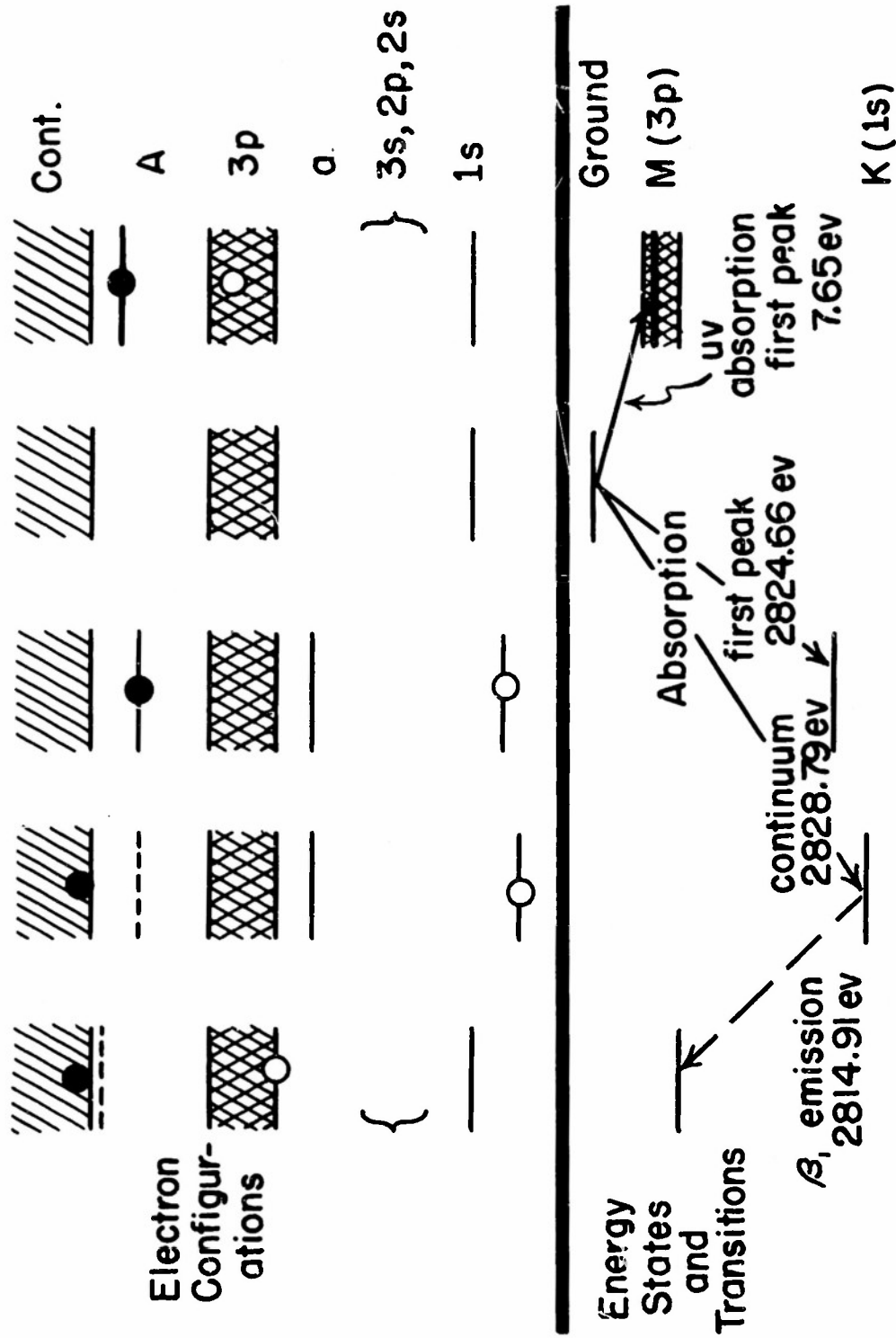


Fig. 6. Emission and absorption in KCl. For simplicity, the B, .. and b, .. levels are omitted. Two 1s (or K) states are indicated; only one is significantly involved in x-ray emission but many more than two are involved in absorption. Two (or more) 3p (or M) states are believed to be involved in x-ray emission and one of them in ultra-violet absorption. The energies listed are for chlorine, referred to the β_1 wavelength 4394.91 xu (Valasek, ref. 16). This chart omits many electronic configurations and energy states that may be present in crystalline KCl.

the discrete levels, a, b, c and A, B no longer exist, and the final electron configuration is one with a vacancy in the 3p band²². But the vacancy position in the band, and the energy and width of the final state, depend upon whether the electron that jumped to the 1s hole came from, say, an a level or from the 3p band itself.

If the electron came from the 3p band, the final hole may be anywhere in the band, the statistical position being determined by the product of the transition probability and the density of states in the band. In this event, the β emission should be broad, as discussed earlier, Fig. 1. It is believed that this transition is part of the observed faint unresolved structure on the high energy side of the β_1 line for either chlorine or potassium, Fig. 3, but it is not the strong β_1 line itself. This 3p band emission corresponds to a transition in Fig. 6 from column two to column five, arrow not drawn.

If the electron came from the a (or b or c) level, the final hole in the 3p band is located at that part of the band (or bands) from which the a level was extracted during the formation of the initial 1s state. There are theoretical reasons for believing that the extraction is from the bottom of the band (or bands)²⁰, and, if so, the energy of the final state is at the lower limit of the broad energy smear corresponding to the band of solid-state 3p states. This energy position is in agreement with the transition yielding the observed β_1 line if the band

22. Associated with the hole in the 3p band are new A, B levels, new in the sense that an electron in such a level is bound to the 3p hole rather than to the 1s hole. The 3p hole and its bound electron constitute a mobile exciton which has been described by Wannier, ref. 17.

radiation is part of the β_x or β'' complex structure shown in Fig. 3. It may be noted also that experimentally there is no apparent unresolved structure on the low energy side of the β_1 line.

The extraction of the \underline{a} level must be essentially the same for all atoms suffering the 1s vacancy, since this extraction is an inherent part of the formation of the 1s state and the 1s state is experimentally sharp²³. This means the final state must be very narrow in agreement with the observed narrow β_1 line.

The probability that an outer electron will jump into the 1s vacancy is proportional to the overlap of the outer electron wavefunction with the 1s wavefunction. For a photon polarized in the x-direction the transition probability $P_{1s \rightarrow \underline{a}}$ is proportional to

$$e^2 \left| \int \psi_{\underline{a}}^* x \psi_{1s} d\tau \right|^2.$$

Because the wavefunction of the \underline{a} level electron is localized about the 1s site, the overlap of $\psi_{\underline{a}}$ and ψ_{1s} is relatively large, and therefore $P_{1s \rightarrow \underline{a}}$ is perhaps larger than $P_{1s \rightarrow 3p}$ band. If so, it is in agreement with the observed strong β_1 line. The ratio $P_{1s \rightarrow \underline{a}}/P_{1s \rightarrow 3p}$ band refers, of course, to areal intensities, not peak intensities.

23. In a metal, the final vacancy in the valence or conduction band, following a transition from the valence \underline{a} level to the 1s hole, may "bubble up" toward the top of the valence band by a series of radiationless transitions in which a conduction electron is raised to an empty conduction level in each transition step. (See P.T. Landsberg, Proc. Phys. Soc. A 62, 806 (1949). If the bubbling process is fast, the final state in \underline{a} -type emission should be wider than for an insulator). In a filled band, metal or insulator, the bubbling is greatly inhibited or prevented.

We conclude that this transition assignment for β_1 , viz., an a electron jumps to the 1s vacancy, is probably correct. This transition is drawn in Fig. 6.

Complex Structure Accompanying β_1 . We have already implied that the 3p band emission is part of the high-energy structure accompanying β_1 . Perhaps also in this structure is the line arising from a p electron jumping to the 1s vacancy, but it is possible that this transition is relatively too improbable to be observed. It seems more likely that the usual "satellites" -- double inner ionization lines, e.g., $1s3s \rightarrow a3s$ -- are superposed on the 3p band emission. Satellites in this region have been reported for several neighboring elements, and for various compounds^{24,25}. Our knowledge of satellites (at least K-series satellites) is very meager, both experimentally and theoretically²⁶.

24. E.g., H. Tazaki, J. Sci. Hiroshima Univ. A3, 321 (1933), A4, 185 (1934), A6, 299 (1936), and A10, 73 (1940), and S. Kawata, Kyoto Coll. Sci., Mem. 13, 383 (1930).

25. E.g., J. Valasek, ref. 16

26. The current view (e.g., see F.R. Hirsh, Rev. Mod. Phys. 14, 45 (1942)), although qualitatively substantiated for only some satellites, favors the double inner ionization theory. The competing theory, the Richtmyer "double electron jump", is expected to be more favorable as the coupling between inner and outer electrons get stronger, as with decreasing atomic number. The wavelength position of a "double jump" satellite would seem to be the more sensitive to variations in the solid state, and if the second jump involves a broad band of states (e.g., $1s3s \rightarrow a3p$ or $1s3p \rightarrow a3p'$ where $3p'$ is a higher hole in the band than the initial 3p hole) the satellite line should be broad. Satellites appear to be only slightly broader than the parent lines (e.g., see Parratt, ref. 21, and C.A. Randall and L.G. Parratt, Phys. Rev. 57, 786 (1940)), but this appearance may be a mere consequence of arbitrary resolution into components.

Most K β satellite studies for low atomic numbers have been with badly overexposed photographic plates, studies carried out for the purpose of detecting and measuring wavelength positions only.

We can't yet distinguish clearly between the broad $1s \rightarrow 3p$ band emission and satellites. But if the $3p$ band emission is an appreciable fraction of the observed intensity, then, to be consistent with the β_1 interpretation, we must readjust the background in Fig. 3 to decrease the β_1 component intensity at its peak, shift its peak slightly to lower energy, and thereby leave some $3p$ band intensity to overlap the β_1 peak position by half the width of the $1s$ state. Then, the suggested line close to β_1 is considerably more pronounced and is obviously a narrow component, perhaps a \underline{p} line or a satellite. This background readjustment, which could leave the width and shape of β_1 unaltered, has not been done because of an unknown relative intensity and shape assignment for the $3p$ band emission.

The potassium β_5 line may be a satellite line. This line is found at an energy position 11.68 ev higher than the β_1 peak and -12.96 ev from the continuum, see Fig. 2. Its numerical subscript implies that it is the quadrupole line $1s \rightarrow 3d$ as traced down from elements of higher atomic number, but this is not reasonable. Valasek²⁵ suggested that the β_5 line may arise in a cross-transition $K^+1s \rightarrow Cl^-3p$, but the transition probability of this assignment is probably low since, as viewed by the K^+1s hole, the Cl^-3p wavefunction has s- or d-type symmetry²⁷. We do not

27. O'Bryan and Skinner, ref. 1, also discuss cross-transitions but point out the "symmetry-interchange" effect. However, the emission bands they attribute to cross-transitions have an amazingly high relative intensity.

now propose an interpretation of $K^+ \beta_5$ but would say that, experimentally, it is a broad line (or lines) with large asymmetry (the peak is on the low energy side of the center of the line).

Many β_1 satellite lines (8 or more for potassium and 12 or more for chlorine) have been reported by various observers using overexposed photographic plates. The reality of some of these "lines" is in some doubt (they may be just individual grains in the photographic emulsion), but others may involve the characteristically solid state states, both narrow and broad. We have mentioned only a few of the obvious possible states.

Absorption Spectra

The experimental absorption curves are shown in Fig. 2. In terms of the previous discussion, we feel impelled to interpret the first absorption peak as the transition indicated in Fig. 6, viz., the one in which the 1s electron goes to the A level²⁸. Also, it appears eminently reasonable that the second absorption peak comes about when the 1s electron is placed in the B level.

Widths of Final States. To check these presumptions, we shall first inquire about the final state widths. In each case, if the absorption contour is resolved into two absorption lines and a complex continuum, the full width at half maximum of the first line cannot be much different than 2 ev before correction for the spectrometric resolving power, and 1.6 ev after correc-

28. The association of the first absorption peak with a discrete exciton-type level is not new; e.g., see R. Landshoff, Phys. Rev. 55, 631 (1939), and Y. Cauchois and N.F. Mott, Phil. Mag. 40, 1260 (1949).

tion. The shape of the observed contour above the line (discussed in detail later) is sufficiently close to classical dispersion, Eq. (1), that we may subtract the width of the 1s state to obtain the width of the final state. The resulting width is about 1.2 ev for chlorine and 1.0 ev for potassium. Similar argument about the second absorption peak, although less satisfying because of the greater amount of overlapping structure, brings a similar result. These widths are less than the predicted width of any band in the continuum, and this fact, together with the shapes of the absorption lines, supports the A, B level assignments.

Incidentally, since most of the final state width in the absorption line transition is due to the A (or B) level, we can see now that the 1s state containing an occupied A (or B) level (e.g., column three of Fig. 6) cannot be the initial state for the narrow β_1 emission.

In the transition giving rise to the A (or B) absorption line, the final state is appreciably wider than the observed 1s absorption edge for metallic potassium. This fact is strong evidence for the contention that the A, B levels do not form in metallic potassium. This conclusion was previously but independently arrived at from the arguments that (a) the conduction electrons in a metal quickly move in to screen the regions more distant from the vacancy site, and (b) there is no observed pronounced structure near the K absorption edge of a metal^{2,28}.

The Bottom of the Continuum. The position of the bottom of the continuum is not readily recognizable in the observed contour for either chlorine or potassium, Fig. 2, but we would like to know this position in each case.

The theoretical calculation of the energy difference between the 1s states having the electron (a) in the A level or (b) at the bottom of the continuum, i.e., the energy states of the second and third columns of Fig. 6, is not an easy one. A simple, qualitative result, however, may be obtained from the hydrogenic relation

$$\Delta E_{n=1} \doteq \frac{m_r}{m_e} \frac{R}{n^2 \epsilon_0^2} \doteq \frac{13.58}{(2.13)^2} \doteq 3 \text{ ev}, \quad (3)$$

where m_r is the reduced mass of the coupled 1s hole and the A electron, m_e the electronic mass, R the Rydberg, $n = 1$ for the lowest hydrogenic state, and $\epsilon_0 = 2.13$ the high frequency²⁹ dielectric constant. For the B electron, $n = 2$, and $\Delta E_{n=2} \doteq 0.75 \text{ ev}$. Each of these calculations presumes the spatial extent of the A or B wavefunction is large, sufficient to justify using the normal bulk value of the dielectric constant³⁰. The wavefunction extent indicated in Fig. 5 is perhaps not quite this large, especially for the A electron³¹. With a limited A orbital size, ϵ_0 is a

29. An interesting aside question arises as to whether the electrons have time to move (in polarization of the medium) during the extremely short lifetime of the 1s vacancy. For chlorine, this time (footnote 18) corresponds to a frequency of about $(4/\Delta T) \simeq 2.7 \times 10^{15}$ cps, or to a radiation wavelength of about 1100 Å. For potassium the corresponding wavelength is about 680 Å. Presumably, one should use the dielectric constants corresponding to these wavelengths.

30. N.F. Mott and R.W. Gurney, Electronic Processes in Ionic Crystals (Oxford, 2nd Ed., 1948).

31. Eq. (3), applied to the case of the A electron coupled with a 3p hole (column five in Fig. 6), gives $\Delta E_{n=1} = 1.8 \text{ ev}$, if the ratio $m_r/m_e = 3/5$ which seems reasonable for the mobile exciton (assuming that the same dielectric constant applies). This ΔE agrees with the separation between the peaks observed in ultraviolet absorption for KCl, ref. 30. Although the extent of the A wavefunction associated with the 3p hole is not the same as with the 1s hole, we may evidently derive some confidence from the simple, qualitative calculation.

little closer to unity, and $\Delta E_{n=1}$ is correspondingly larger than the calculated 3 ev. In this connection, we note that the observed difference between the A and B absorption peaks is 3.9 ev for chlorine and 3.5 ev for potassium.

It may also be pertinent to remark that the bottom of the continuum in crystalline KCl is normally thought of as the bottom of the 4s chlorine band. The potassium 1s electron may go happily (by the selection rules) to the bottom of this band because of the symmetry-interchange effect, but the chlorine 1s electron may prefer to go to a higher level having p-type symmetry near chlorine and s- or d-type near the potassium sites. (In general, the symmetry types in a band become mixed as one progresses up from the bottom, but at and near the bottom of an s-type band, the symmetry remains pure s.³²) Hence, the 1s absorption continuum for potassium may be a little lower than for chlorine, and the shape of the absorption continuum may be different in the two cases.

The energy position of the bottom of the continuum is arbitrarily taken as 4.13 ev and 3.2 ev as measured from the first absorption peak for chlorine and for potassium, respectively, as

32. F. Von der Lage and H.A. Bethe, Phys. Rev. 71, 612 (1947).

indicated in Fig. 2.³³

This choice in each case, we might say, makes more palatable the observed relative intensities of the first and second absorption peaks. The relative height of the second peak for potassium is reduced, as a component absorption line, when the continuum background is subtracted.

The chosen energy position for the bottom of the continuum does not agree in either case with any previously reported position of the K absorption edge³⁴. Although fine structure has been commonly observed near the edge, there have been very few satisfying attempts to interpret it. The usual pragmatic definition of the position of the edge places it about half way up the first abrupt

33. If we consider the A, B, ... levels for potassium as the vestiges of the optical 4p, 5p, ... levels, they may bear some relation to the levels in singly ionized calcium (as in the analysis for gaseous argon, ref. 2). From the optical atomic spectroscopic data, the Ca II 4p→5p separation is 4.37 ev, 4p→6p is 6.10 ev, and 4p→∞p is 3.73 ev. Although each of these separations comes within 1 ev of a suggested peak in the observed absorption contour, the agreement beyond 5p is probably sheer coincidence. The atomic continuum is broadened and altered in forming the solid state, but it seems possible that the 5p or 6p excitation level in KCl may possibly be above the bottom of the continuum, as stated earlier.

The "atomic" interpretation of the first and second absorption peaks may also seem plausible in other work with solids. E.g., see Stephenson, Krogstad and Nelson, Phys. Rev. 84, 806 (1951), and D.H. Tomboulion and E.M. Pell, Phys. Rev. 83, 1196 (1951). Although Tomboulion and Pell's structure is for aluminum, which when pure is a good metal for which no A or B level is believed to form, those Al atoms responsible for the observed absorption maximum are probably embedded, and more or less widely separated, in the non-metallic substrate. The observed large width of the absorption maximum may well be the effect of the various separations between Al atoms frozen in the substrate as the aluminum "film" built up in condensation.

34. E.g., see A.E. Lindh, Handbuch der Experimental Physik, Rontgenspektroskopie (Akademische Verlagsgesellschaft M.B.H., Leipzig, Vol. 24, Part 2, 1930), and Y. Cauchois and H. Hulubei, Longueurs d'Onde des Emissions X et des Discontinuites d'Absorption X (Hermann & Cie, Paris, 1947).

absorption rise³⁵ regardless of the kind or amount of fine structure present.

Shape of Absorption Line. A careful look at the shape of the first absorption line for either chlorine or potassium shows it to be very unusual. The low energy side of the line falls much farther below the classical dispersion shape than does any reasonable x-ray line. Furthermore, the shape near the peak of the chlorine absorption line is strangely asymmetric and strongly suggests multiplet structure.

The A level must have p-type symmetry, but, as viewed by neighboring atoms, the symmetry is s- or d-type. Perhaps the interactions with the neighboring atoms causes the p-type A level to be split into several discrete levels (some being degenerate because of symmetry), and we may expect the absorption lines each to be a close multiplet. (Such splitting is of negligible importance in the a levels.)

Also, the thermal vibrations of the lattice result in an apparent splitting of the A (or B) levels. Although the lifetime of the 1s vacancy is very short compared with the time of a vibration cycle, each atom having a 1s vacancy is caught in a different part of the cycle. Hence, statistically, the A level is really a band of infinitesimally closely spaced lines.

Either or both types of splitting mentioned above may justify an arbitrary resolution of the A and B absorption lines into

35. The discrepancy arising from an attempt to interpret the absorption structure is clearly discussed in the case of gaseous argon, see ref. 2.

components each of which has a reasonable width and shape and whose sum equals the observed contour. Such resolution is not indicated in Fig. 2, however, because of the uncertainty of the bottom position and shape of the continuum.

Base Width of the 3p Valence Band. In ultra-violet absorption, two peaks are observed with KCl, one at 1620 Å (7.65 eV) and the other at 1310 Å (9.64 eV). The first peak is interpreted³⁰ as corresponding to the transition indicated in Fig. 6, the second to the transition in which the 3p electron is ejected to the continuum. (It is assumed³⁰ that the B level, associated with a 3p hole, is at the bottom of the continuum.) The 3p hole in the final state is taken at the maximum of the density of states, a position about 3/4 of the way along the base width of the band as sketched in Fig. 6.

Then, if the energy contribution of the uv A level can be taken as about 1.3 eV less than that of the chlorine x-ray A level, we can deduce an approximate value for the base width of the valence 3p band by the following relation, using energies given in Figs. 2 and 6:

$$(3/4)W_{3p} \doteq 13.88 - 4.13 - 7.65 + 1.3$$

$$W_{3p} \doteq 4.5 \text{ eV (base width).}$$

This value is in good accord with the expected width³ although both values contain some poorly evaluated guesses.